Overview of the ZECA (Zero Emission Coal Alliance) Technology

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Abstract

We discuss a novel, emission-free process for producing hydrogen or electricity from coal. Although we focus on coal, the basic approach is compatible with any carbonaceous fuel. The process uses cyclical carbonation of calcium oxide to promote the production of hydrogen from carbon and water. The carbonation of the calcium oxide removes carbon dioxide from the reaction products and provides the additional energy necessary to complete hydrogen production without the need for the combustion of carbon. The calcination of the resulting calcium carbonate is accomplished using the high temperature waste heat from solid oxide fuel cells, which generate electricity from hydrogen fuel. Converting waste heat back to useful chemical energy allows the process to achieve very high conversion efficiency from fuel energy to electrical energy. As the process is essentially closed-loop, the process is able to achieve zero emissions if the concentrated exhaust stream of CO_2 is sequestered. Carbon dioxide disposal is accomplished by the production of magnesium carbonate from ultramafic rock. The end-products of the sequestration process are stable, naturally-occurring minerals. Sufficient high quality ultramafic deposits exist to easily handle all the world's coal.

Introduction

Fossil energy is the backbone of the world energy market and the motor of modern economies. Yet, in spite of its obvious importance, the entire fossil energy sector is threatened by concerns about carbon dioxide accumulating in the air. At the same time there is currently no cost-competitive alternative energy source capable of meeting present, let alone future world energy demand.

Zero emission coal technology would provide low cost, clean, and copious fossil energy for centuries to come and hence a solution to this dilemma. The 1960's worldview of a globe with rapidly diminishing, scarce resources has proven incorrect. Since the Club of Rome made their doomsday predictions, resources of all kinds have been demonstrated to be more plentiful and have become lower in cost. There is a direct correlation between those countries with healthy, prosperous populations and the availability and use of energy. The challenge is not to limit the use of energy or other resources, but to provide access to enough reasonably priced and clean energy to allow the world population to achieve a standard of living comparable to that of the world's prosperous countries in an environmentally responsible manner.

Fossil energy resources are vast. Coal reserves alone are sufficient to last for hundreds of years, even with greatly increased world energy consumption rates. The carbon available in the form of fossil fuels is shown in Fig. 1. Also shown are the amounts of carbon currently stored in natural reservoirs that are often proposed as sinks for the CO_2 produced from the combustion of fossil fuels. Clearly, fossil carbon reserves dwarf the commonly touted natural sinks for carbon dioxide. The only possible exception to this is the ocean, which represents a vast carbon reservoir. Unfortunately, on the time scale of a few centuries the capacity of this reservoir to take up additional carbon is also limited. CO_2 enters the ocean yielding bicarbonate, carbonate and hydrogen ions, which lower the pH of the ocean. On the order of 1000 Gt of carbon entering the ocean in the form of CO_2 is sufficient to lower the pH of the entire ocean by 0.3 if fully dissolved and mixed. Only over long time scales, will the additional dissolution of calcium and magnesium silicates neutralize the carbonic acid that is formed by the dissolution of CO_2 in the water. Without neutralization, the oceans will acidify. With rising atmospheric CO_2 levels, ocean surface waters will acidify in any case, as they are in equilibrium with atmospheric CO_2. Doubling the
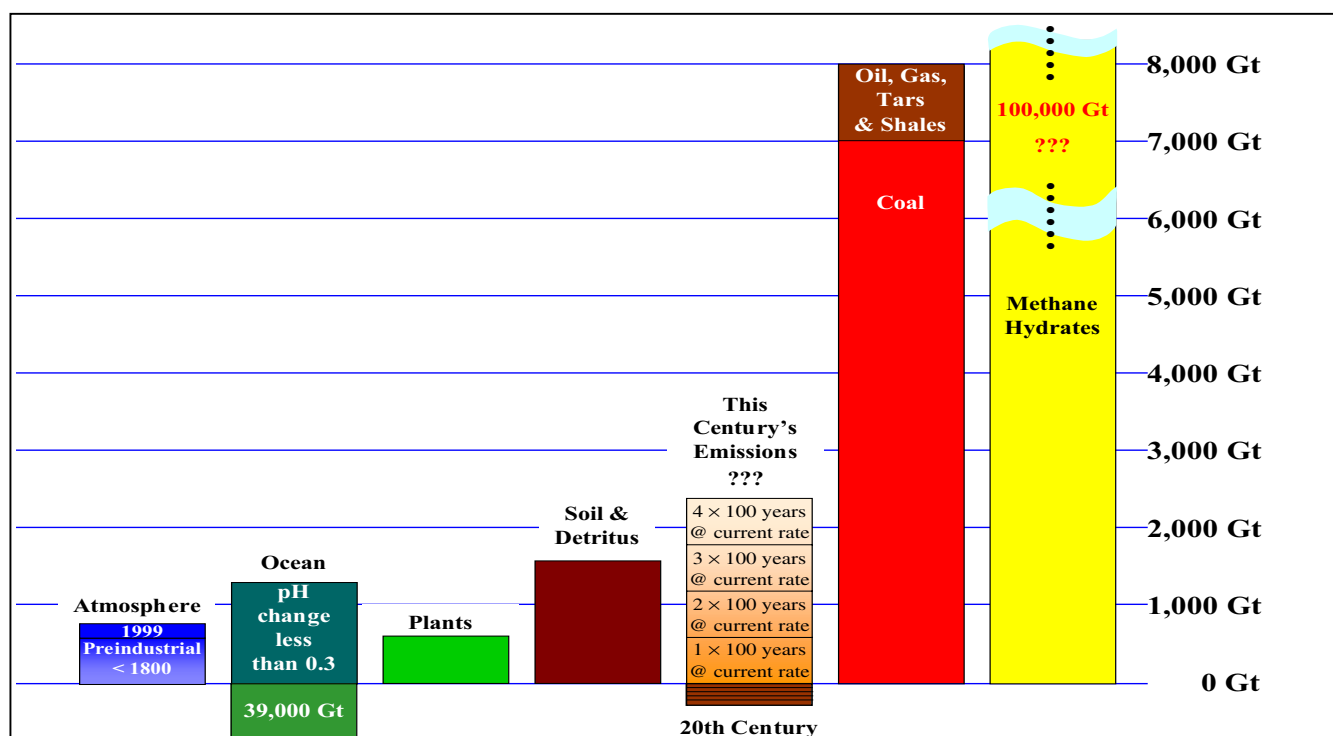
Figure 1: Size of natural carbon pools compared to fossil fuels reserves and to potential emissions in the new century. For the emissions we show 4 blocks of 600 Gt each. At constant emissions, the new century would see 600 Gt of carbon emitted to the atmosphere. The individual blocks below the 0 Gt line in the 20th Century region represent 100 years of emissions using the emission rate at the beginning of that century. Total emissions during the 20th century are given by 5 such blocks. At present, energy consumption doubles every 28 years. The potential for increase is even larger. The scale set in this figure is however completely dwarfed by the amount of carbon estimated to be stored in carbonate rocks ($\geq 40,000,000$ Gt).[1]
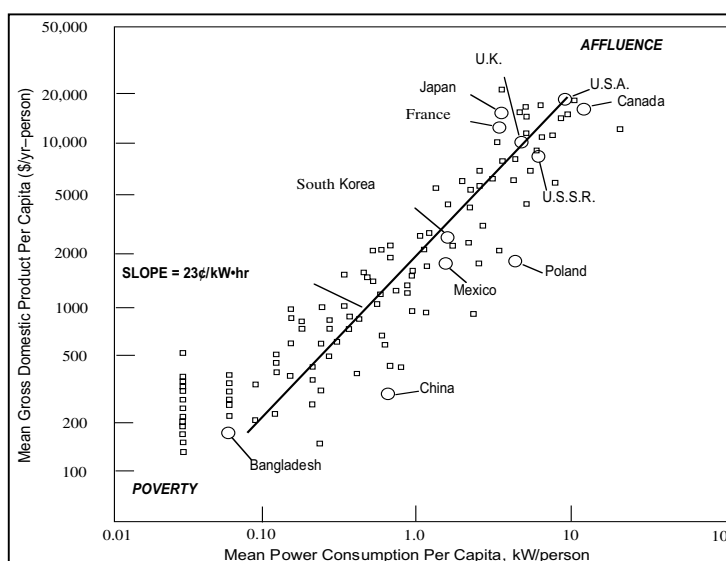

Figure 2: Per capita GDP versus per capita energy consumption for members of the United Nations. Taken from R. G. Watts, "Engineering Response to Global Climate Change." Lewis Publishers. New York. 1997.

level of CO_2 in the air will change the surface water pH by 0.3. This may pose a threat at least comparable to that of global warming.

The potential for increased world energy consumption is very large. Energy consumption translates directly into economic well-being and prosperity, which bring with them improved health, security, and world stability. The relation between per capita gross domestic product (GDP), which is a measure of wealth, and per capita energy consumption is shown in Fig. 2. Today, the per capita energy consumption in the wealthier nations is about 5 times higher than the world average, as is their standard of living. The rest of the world is moving to our standard of living. We cannot deny the rest of the world the same prosperity we enjoy today and expect international stability to be maintained.
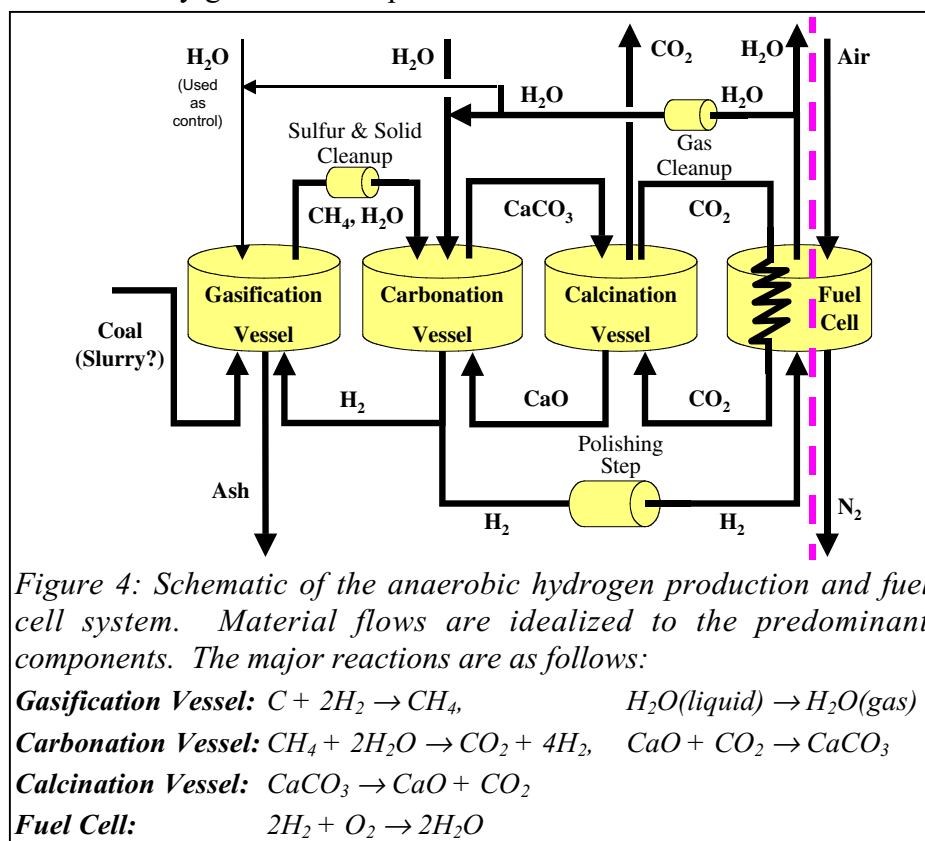
When this factor of 5 disparity is coupled with an expected doubling of the world's population in the next century, a factor of 10 increase in energy consumption is not difficult to imagine. In addition to improved standards of living, energy and wealth provide the means of achieving a clean environment. The dirtiest water and air are not found in the rich countries, rather they are found in the developing nations. As pollution is rapidly becoming a global issue, worldwide prosperity should be viewed as the solution to the problem, not its cause.

Figure 3: Schematic of the zero emission coal process.
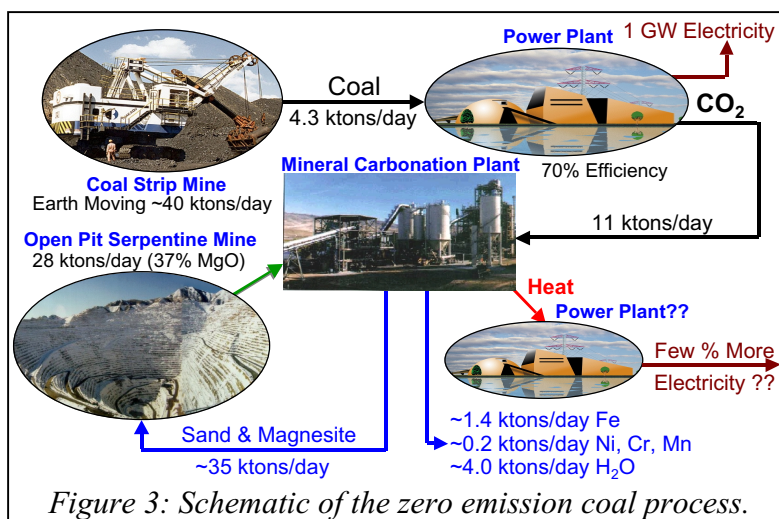
The Technology

Los Alamos National Laboratory has led the development of the zero emission coal technology that is being pursued by the Zero Emission Coal Alliance (ZECA). ZECA is an alliance of industrial, government, and research institutions pursuing a technology for generating hydrogen and/or electricity from coal in an emission-free manner and with very high efficiency. The process generates a pure stream of CO_2 that is disposed of permanently using an industrial process that forms mineral carbonates. Sufficient raw materials in the form of magnesium silicates exist to easily handle all of the world's coal. The recovery of these silicates disturbs a smaller area than is already used to supply the coal.

The full process is illustrated in Fig. 3 and involves a number of integrated, yet distinctly separate modules. Coal is used to generate electricity in a highly efficient zero emission coal gasification plant that naturally generates a separate waste stream of concentrated CO_2 containing all the carbon brought into the process as coal. The CO_2 is transferred to a mineral carbonation plant where it is reacted with magnesium silicates, preferably serpentine or peridotite rock. The magnesium carbonate and silica end-products are returned to the serpentine mine. The end-products are stable thereby guaranteeing permanent sequestration of the CO_2.

Figure 4: Schematic of the anaerobic hydrogen production and fuel cell system. Material flows are idealized to the predominant components. The major reactions are as follows:

Gasification Vessel: $C + 2H_2 \rightarrow CH_4$, $\qquad H_2O(liquid) \rightarrow H_2O(gas)$

Carbonation Vessel: $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$, $\quad CaO + CO_2 \rightarrow CaCO_3$

Calcination Vessel: $CaCO_3 \rightarrow CaO + CO_2$

Fuel Cell: $\qquad 2H_2 + O_2 \rightarrow 2H_2O$

Figure 4 shows an outline of the zero emission coal power plant. The figure shows a schematic of the anaerobic hydrogen production, which integrates coal gasification, hydrogen production via calcium oxide carbonation, and limestone calcination incorporating a fuel cell system. The anaerobic hydrogen production process is an industrial, elevated

temperature process that requires no air (hence anaerobic), involves no combustion, and requires no heat input. Aside from the coal, the process requires only water and CaO as inputs, the latter two being continuously recycled. The process is a variant of the proven CO_2 gas acceptor process.[2] In addition to our work, several other groups are also employing variants of this process to produce hydrogen from a variety of carbon-based fuels.[3, 4]

In Fig. 4, the material flow is represented in an idealized schematic way, emphasizing the dominant compounds produced in each step. Coal enters the gasification vessel either dry or as a slurry and is then gasified with hydrogen. In contrast to the coal-based water-gas shift-reactions and steam reforming, hydrogasification of carbon to methane is exothermic, thereby avoiding the need for external heat in the gasification process. By injecting some water or steam into the gasifier, one can quench the heat released and maintain a constant temperature in the gasifier vessel. (The quenching with water can be achieved either by driving a limited amount of the endothermic water-gas production reaction or by the generation of steam in the case of liquid water injection.) By transforming the carbonaceous compounds of the fuel into gaseous forms, the gasifier separates out the ash, leaving it behind in the gasification vessel. The carbon, which is now in the form of volatile carbon compounds, enters the carbonation vessel where it reacts with water to form CO_2 and hydrogen. The CO_2 is continuously removed from the reaction zone by its reaction with CaO to form $CaCO_3$. In principle, the mixture of liquid water, steam, and volatile hydrocarbons that reacts in this vessel neither consumes nor generates heat. This follows from the observation that the net reaction (1) in the gasification and carbonation units is energetically neutral. Thus, the total heat release in the units is zero. Since we adjusted the first vessel to have zero heat release the second one must also have zero heat release. Of course, to the extent that water enters the vessels as steam, the net reaction becomes exothermic. This provides an avenue to compensate for the inevitable heat losses that will occur in a realistic implementation of the process.

$$CaO + C + 2H_2O(liquid) \rightarrow CaCO_3 + 2H_2 + 0.6 \text{ kJ/ mol C} \tag{1}$$
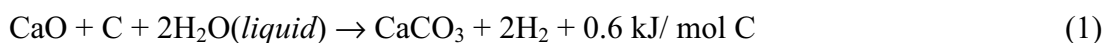
The gaseous product of the carbonation vessel contains four moles of hydrogen per mole of carbon that is introduced into the gasification vessel. Half of this hydrogen stems from the hydrogen in the methane that is generated in the gasification vessel. This hydrogen is recycled to the gasification vessel to gasify more coal thereby closing the coal gasification loop. The other two moles of hydrogen derive from the water. It is this half of the hydrogen that is the true product. Because the hydrogen production reaction also took up the heat of carbonation reaction ($CaO + CO_2 \rightarrow CaCO_3$), the hydrogen product stream contains approximately 150% of the energy brought into the process by the carbon. With the provision that total energy must be conserved, conceptually all of this energy from the hydrogen is available for electricity generation. However, the laws of thermodynamics dictate the maximum conversion efficiency that can be achieved and practical considerations further limit what can be achieved in practice. Of the initial energy available for electricity generation, any losses due to conversion processes end up as heat. The maximum temperature of this by-product heat is dependent on the conversion process and is again dictated by the laws of thermodynamics. For some processes, the temperature of the rejected heat is quite low as in typical power generation systems (*e.g.* steam plants, etc.). Such processes are indirect conversion processes that involve the use of heat to perform the conversion. In order to achieve high conversion efficiency in these processes, the laws of thermodynamics demand that the rejected heat available at the end of the process must be at low temperature and, therefore, unavailable for further electricity generation. In contrast, in direct conversion processes, such as those used in fuel cells, there is no such limit as to the temperature of the rejected heat, which is potentially available at high temperatures. For solid oxide fuel cells (SOFC), the waste heat is emitted at the operating temperature of the fuel cell, about 1050 ^{o}C. At such high temperatures, this waste heat can be usefully employed and thus need not be lost.

Recall that in our process, the hydrogen product stream had about 150% of energy brought in by the carbon of the coal. Thus even if the electrical generation process is only 50% efficient, a typical number for solid oxide fuel cells, one still converts 75% of the energy brought into the process by the carbon into electricity. Energy must of course be conserved. The additional energy (50%) was brought into the hydrogen production reaction by the CaO to $CaCO_3$ reaction. Unless one has a free source of CaO, which typically is not available, the energy loan from the carbonation reaction must be repaid. This is done in the calcination vessel making use of the waste heat generated by the SOFC. The calcination reaction that occurs in the third vessel requires an amount of heat that matches the heat released in the carbonation reaction. The heat must also be provided at sufficient temperature, about 900 ^{o}C, in order to drive the calcination reaction. Heat at this temperature is available from the fourth unit, the SOFC.

For thermodynamic reasons, high temperature hydrogen consuming fuel cells cannot avoid turning roughly one third of the energy of the oxidation of hydrogen into waste heat. (In actual practice, this number turns out to be about 50%.) However, as noted above, SOFCs operate at a temperature where this waste heat can be utilized to calcine the $CaCO_3$. This "waste heat" is thereby turned back into usable chemical energy, which is carried by the CaO. By closing the CaO loop one also maintains the energy balance of the system.

Since the process utilizes the waste heat of the fuel cell to generate additional hydrogen, it is highly efficient. In the theoretical limit of a pure carbon input, zero heat losses, and optimal performance of the fuel cell the efficiency of converting the heat of combustion of the carbon fuel into electricity would be 93%. Additional losses occur because heat will escape from the vessels and because a realistic conversion efficiency of a fuel cell is less than the thermodynamically allowed limit. Nevertheless, a very high conversion efficiency, on the order of 70%, for the conversion of coal energy to electrical energy should be achievable. Thus, compared to standard processes, the new process generates substantially less CO_2 for the same amount of electrical energy delivered. This in turn greatly reduces CO_2 disposal costs per unit of electricity.

If instead of the energy one tracks the free energy of the system one sees immediately that the free energy of the carbon is gradually reduced. The oxidation of hydrogen at 1050°C results in a value of 0.7 for $\Delta G/\Delta H$. For carbon, the equivalent ratio is 1.02. Thus, the free energy of the system is somewhat reduced suggesting an increase in entropy as demanded by the second law of thermodynamics.

The process is economically attractive in that it eliminates all emissions to the air. The process has no smokestack, as there is no combustion of the coal. Thus the ash from the coal is fully contained, making compliance with ever-tighter restrictions on particle emissions straightforward. A small amount of added calcium oxide or calcium carbonate is used to capture the sulfur in the coal. The sulfur is pulled out of the reaction vessels in a solid form, thereby also eliminating hydrogen sulfide or SO_X emissions. Additionally, the reducing conditions inside the hydrogen production vessel do not lead to the formation of NO_X, and since there is no combustion involved, NO_X emissions are pushed to zero. Finally the CO_2 generated in the hydrogen production is initially extracted as a solid, before being converted to a pure gas stream. As this is an integral part of the hydrogen production process, no additional expenses are incurred in producing a concentrated CO_2 exhaust stream.

Fig. 4. also shows that the process is essentially a closed loop. SOFCs transport oxygen, thereby acting as oxygen separation membranes. Thus the hydrogen side of the fuel cell is never exposed to air, which means that the product (water) side of the fuel cell is not diluted with air (nitrogen). Any hydrogen that passes through the fuel cell, without being consumed, is simply recycled for a second pass. The closed nature of the process greatly simplifies the removal of any remaining contaminants introduced by the coal. An effectively closed-loop system allows one to build up internal byproducts to a level where they can be easily handled. (The internal levels must of course remain at concentration values below which they become detrimental to the operation of the system components.) Consider for instance, a gaseous
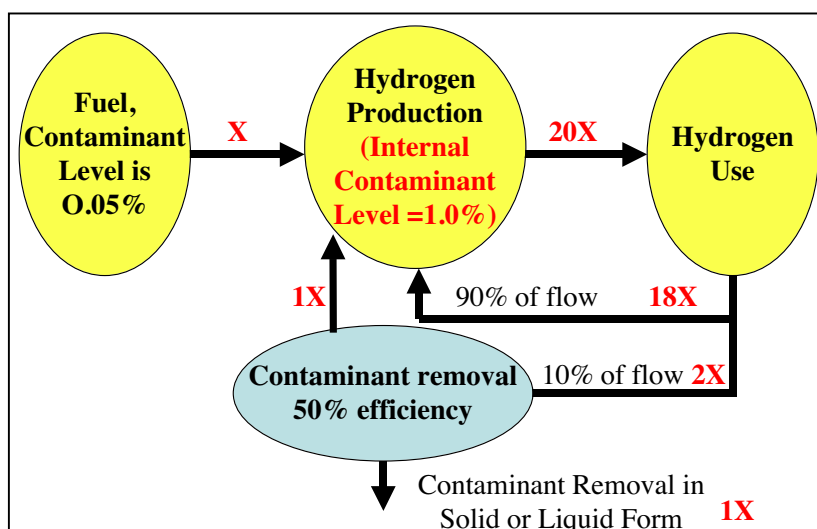
Figure 5: A sketch of a conceptual representation of a slip-stream process for removing all the contaminants introduced by the coal. The process fully removes all the contaminant introduced although in a single pass it is rather inefficient.

impurity in the coal that comes in at say a 0.05 percent level as shown in Fig. 5. The internal level of this impurity will continue to build up until one attempts to extract it. If the gas loops the system twenty times, the internal level of this contaminant would build up to the 1% level. At that point, if one runs a slipstream that contains 10% of the total gas flow through an extraction system that only has a 50% single-pass removal efficiency for the contaminant, one is still removing as much contami nant as is being introduced by the coal in a single pass. In this manner one can use relatively inexpensive contaminant processing while still removing all the contaminants introduced by the coal.

This is in contrast to present day systems, which vent directly into the atmosphere and where, therefore, removal efficiencies must be extremely high (and most likely expensive) to reach typical part per million emission levels.

The CO_2 will be permanently disposed of by reacting it with abundant naturally-occurring minerals to form harmless stable mineral solids that will not leave a CO_2 legacy for future generations. This mineral carbonation concept is being developed by a collaboration that includes Los Alamos National Laboratory, the Albany Research Center, Arizona State University and the National Energy Technology Laboratory. The process reacts CO_2 with magnesiu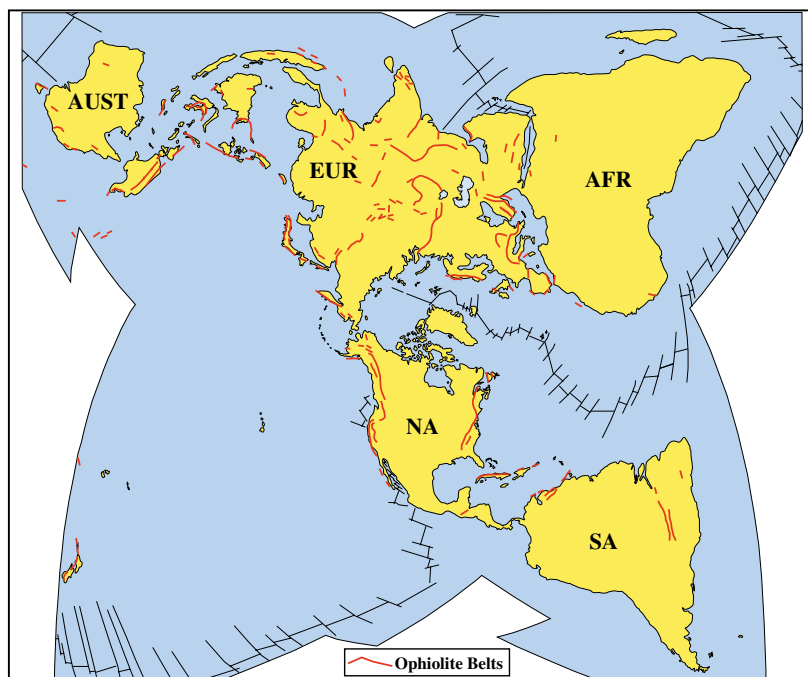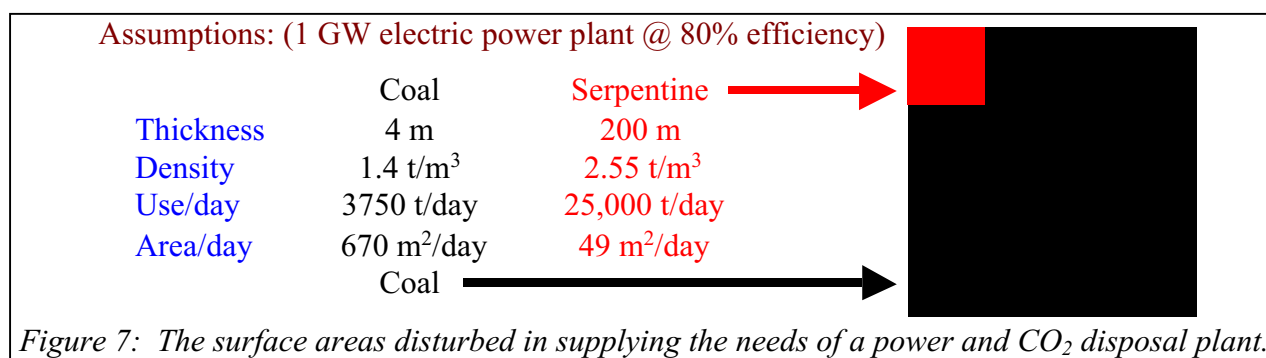m rich silicates (serpentine or olivine) yielding magnesium carbonate (the magnesium analog of lime-stone), silica (quartz), and possibly water. The end-products are all naturally-occurring and the reaction is actually part of the natural geological carbon cycle. The reaction that produces the magnesium carbonate also generates energy (heat) that could potentially be harvested. The magnesium carbonate product is thermo-dynamically favored and hence the disposal is truly permanent.

The starting magnesium silicates exist in vast, rich deposits worldwide, as is shown in Fig. 6. A single deposit in Oman contains over 30,000 cubic kilometers of magnesium silicates, which alone could handle most of the world's coal. Taken together, the world's rich magnesium silicate deposits are sufficient to easily handle the entire world's

Figure 6: The world's principal ophiolite belts. (Adapted from W. P. Irwin & R. G. Coleman, USGS, 1974)

Assumptions: (1 GW electric power plant @ 80% efficiency)

	Coal	Serpentine
Thickness	4 m	200 m
Density	1.4 t/m^3	2.55 t/m^3
Use/day	3750 t/day	25,000 t/day
Area/day	670 m^2/day	49 m^2/day
	Coal	

Figure 7: The surface areas disturbed in supplying the needs of a power and CO_2 disposal plant.

coal supply. The operation scale involved is not unreasonable. The required mining operation suitable for a large electric power plant is smaller than that for a large open pit copper mine. Even though the mineral carbonation requires six times the mass of serpentine compared to coal, the surface area disturbed in supplying the serpentine is considerably less than that of the corresponding surface coal mine. The area of serpentine mining is smaller, because serpentine deposits are typically much thicker than coal deposits and serpentine is denser than coal. Figure 7, shows an area comparison for coal mining and serpentine mining.

The end products from the carbonation process would be used to refill the pit. Based on copper ore mining and milling costs, and the likely required plant size for the chemical processing, a disposal cost of $15-20 per ton of CO_2 would not be unreasonable. Even a recent IEA study[5] agrees that the mining, crushing, milling and reclamation costs are low, around $7 to $10 per ton of CO_2. The study noted that the difficulty lies in the design of an efficient chemical process. Simple processes that bring together the CO_2 and the serpentine rock in a direct reaction are potentially very low in cost. If the size of the plant is determined by a residence time of the solids that is on the order of an hour, the containment vessels, even if they are pressure vessels, will add little to the cost of the plant. For an output of one ton of CO_2 per hour a vessel would ideally have to hold roughly 2 tons of serpentine resulting in a size on the order of a few cubic meters. For large vessels the cost is about $1000 per cubic meter. Ten percent interest on a capital cost of $10,000 would results in hourly charge of roughly 10 cents. Containment vessel costs add tens of cents to the cost of a ton of CO_2. Thus, even allowing for many other costs, $10 per ton of CO_2 from the chemical processing appears to be well within the realm of the feasible. In a recent study, the group at Albany has demonstrated a process that promises a very simple implementation.[6] In effect; CO_2 in contact with olivine or serpentine, water, sodium bicarbonate, and sodium chloride transforms the bulk of the rock into magnesium carbonates and silica. The $NaHCO_3$ and $NaCl$ play the role of catalysts and are not consumed in the process. The Albany process sidesteps the concerns raised by the IEA in their report[5] and suggests an implementation for the mineral carbonation process that including mining would be on the order of $15 to $20 per ton of CO_2. With a power plant operating at 70% efficiency, this would be about 1¢ US/kWh of electricity.

In conclusion, coal has an important and even dominant position in the energy future for the world. It is important that the value of this resource be recognized and utilized. We are confident that the technological solutions exist that will allow the realization of "green" coal, which can be used to ensure a clean world and a long term, prosperous, healthy, and secure global economy.

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